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Magnetic field-assisted pulse chromatography for simultaneous in situ extraction of uranium and lithium from salt lake

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Abstract

Salt lakes represent vast resource reservoirs, and the separation and extraction of metal resources such as uranium and lithium from in-situ salt lake brine can effectively mitigate energy scarcity challenges. This study presents an automated pulsed liquid chromatography separation device employing magnetic field assistance for the efficient extraction of critical metals, including uranium and lithium, from salt lake brine. The device incorporates a unique gas-liquid dynamic pulse injection mechanism and utilizes a 10-meter chromatographic column packed with polymethyl methacrylate pellets (average diameter 1.0 mm) to provide multiple effective separation units, thereby substantially enhancing separation efficiency. The chromatographic column exhibits excellent acid and base resistance. The solution flow rate in the column was 16 mL/min, with a pulse volume of 20 mL per separation cycle. The column maintained structural integrity after undergoing more than 6000 separation cycles with salt lake brine, demonstrating extended service life and excellent recyclability. Through optimization of magnetic field assistance, simultaneous separation and extraction of uranium and lithium from in-situ salt lake brine was successfully achieved using an annular magnet. Experimental results demonstrate a magnesium-lithium separation factor of 1.202 and a uranium-lithium separation factor of 1.088. Theoretically, a solution with an initial magnesium-lithium ratio of 200 can be reduced to 20 through merely 13 separation stages. Control columns employing glass pellets as packing material were utilized to investigate functional group effects and verify liquid membrane formation. The mechanism of ion migration on the packing surface under the synergistic effects of magnetic field and liquid membrane was analyzed comprehensively. The results indicate that pulsed chromatography combined with magnetic field assistance can significantly enhance the simultaneous extraction efficiency of uranium and lithium from salt lakes, thereby providing novel research insights and technical expertise for industrial applications in chromatography and salt lake resource extraction.

Full Text

Preamble

Salt lakes represent a vast treasure trove of resources, and the in situ separation and extraction of strategic metals such as uranium and lithium from brine can effectively alleviate global energy shortages. In this study, we developed an automated pulsed liquid chromatography separation device assisted by magnetic fields for the efficient extraction of these critical metals from salt lake water. The apparatus employs a unique liquid-air-liquid dynamic pulse injection mechanism and utilizes a 10-meter chromatographic column packed with polymethyl methacrylate (PMMA) pellets (average diameter 1.0 mm) to provide multiple effective separation units, dramatically improving separation efficiency. The column exhibits excellent resistance to both acidic and alkaline conditions. Operating at a flow rate of 16 mL/min with a single separation pulse volume of 20 mL, the column has withstood over 6000 pulses of salt lake water while maintaining normal function, demonstrating long service life and good cyclability. By optimizing magnetic field assistance, we ultimately achieved simultaneous separation and extraction of uranium and lithium from in situ salt lake water using a ring magnet configuration. Experimental results show a magnesium-lithium separation factor of 1.202 and a uranium-lithium separation factor of 1.088. Theoretically, a solution with an initial magnesium-lithium ratio of 200 can be reduced to 20 using only 13 separation stages. To examine the effect of functional groups and verify the presence of a liquid film, we compared columns packed with glass pellets. We conducted an in-depth analysis of ion movement mechanisms on the packing surface under the combined influence of magnetic fields and liquid films. The results demonstrate that pulsed chromatography combined with magnetic field assistance can significantly enhance the simultaneous extraction efficiency of uranium and lithium from salt lakes, providing new research insights and technical experience for industrial applications in chromatography and salt lake resource extraction.

Keywords: Pulsed liquid chromatography; Simultaneous in situ extraction; Uranium; Lithium; Salt lake

Introduction

Many countries worldwide have implemented climate policies to reduce carbon emissions, leading to decreased demand for fossil fuels. Lithium, uranium, and other resources are pivotal for transitioning to clean energy and achieving sustainable development [**?**]. Reports predict that global lithium demand will reach 1.93 million tons by 2050, representing a 26.2-fold increase compared to 2023 [**?**]. Meanwhile, terrestrial uranium reserves are estimated at only 7.6 million tons, insufficient to meet long-term production demands. Although approximately 4.5 billion tons of uranium exist in seawater, the extremely complex marine environment and low average concentration of 3.3 µg/L make extraction highly challenging [**?**]. Like seawater, salt lake water is rich in various metal ions, but with uranium concentrations tens or even hundreds of times higher than seawater [?, ?]. Similarly, lithium concentrations are hundreds to thousands of times greater than in seawater. According to the US Geological Survey, global proven lithium resources total about 89 million tons, with over 60% contained in salt lake brines [?]. Therefore, from both resource regulation and environmental protection perspectives, the separation and extraction of strategic resources such as U(VI) and Li from salt lake water is highly promising.

The main methods for extracting uranium from salt lake water include adsorption [?], photocatalysis [?], and electrochemical processes [?]. Currently, adsorption-based uranium extraction from salt lakes has been studied most extensively. Hydrogel and aerogel materials containing amidoxime groups have shown excellent uranium adsorption performance [?, ?]. However, although salt lakes contain high concentrations of metal cations, the ubiquitous presence of microorganisms also affects the practical extraction efficiency of various methods [?]. Consequently, antimicrobial materials have been widely investigated.

Concurrently, lithium extraction from salt lakes has become a research hotspot in academia, with methods including precipitation [?], adsorption [?], solvent extraction [?, ?], membrane separation [?, ?], electrochemical processes [?], and photocatalysis [?]. Essentially all these methods focus on magnesium-lithium separation. Among them, precipitation, adsorption, and solvent extraction have been industrially applied. Whether for U(VI) or Li extraction, the high concentration and diverse species of coexisting ions in salt lakes impose stringent requirements on extraction conditions. Taking the electrochemical method as an example, ideal electrode materials should possess good selectivity, corrosion resistance, and regeneration capability.

Chromatography has become an indispensable technique in analytical and preparative chemistry due to its ability to efficiently separate and purify complex mixtures, especially for substances with similar chemical properties. Building on this foundation, traditional chromatography (liquid and gas chromatography) has been widely applied in detection, analysis, and separation [?], demonstrating extraordinary value in isotope separation and pharmaceutical ingredient analysis. Ye [?] first employed dynamic chromatographic separations to achieve rapid non-equilibrium separation of uranium isotopes. However, chromatography applications must consider various factors such as processing volume, continuity, adsorbent equilibrium variability, desorbent consumption, and column clogging [?, ?].

Currently, most research on element extraction from salt lakes or seawater focuses on single-element extraction, with few experiments achieving simultaneous extraction of two or more elements. Therefore, we designed and constructed a novel pulsed liquid chromatography separation device to achieve simultaneous extraction of U(VI) and Li from salt lakes.

Chromatography, particularly through our pulsed device powered solely by electricity, excels in U(VI) extraction from salt lakes, enabling prolonged stable separation that enhances efficiency by avoiding frequent adsorbent/desorbent addition. Resistant to crystallization blockage and microbial interference, it ensures reliable performance. An external magnetic field further enhances column separation, making the process more efficient and manageable. However, despite pulse chromatography' s throughput advantages over conventional methods, it still falls short of industrial demands, necessitating further research into column packing—a critical factor affecting separation efficiency, stability, lifespan, and effectiveness. While inorganic materials are cost-effective, they lack functional groups, and organic materials often fail under harsh conditions. Addressing these challenges requires ongoing optimization of separation techniques and in-depth study of packing materials to advance chromatography in salt lake resource extraction.

This project explored optimal separation conditions for in situ extraction of U(VI) and Li from salt lakes, achieved multistage separation, and calculated separation factors. We characterized the acrylic packing pellets using Fourier Transform Infrared Spectroscopy (FTIR, model: Thermo Fisher Scientific Nicolet iS20), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS) (model: Hitachi SU8100), and X-ray Photoelectron Spectroscopy (XPS, model: Thermo Scientific K-Alpha). We also discussed the trajectory and separation mechanism of ion motion in the column. The results showed that the pulsed liquid chromatography separation device can effectively, economically, and with low carbon footprint extract U(VI) and Li from salt lake water, demonstrating potential for multiple fields and large-scale industrial application, and providing new ideas for salt lake resource extraction and utilization.

II. Experimental

2.1 Materials

The instruments used in this study include a peristaltic pump (model BQ80S+FZ10-CE), an inductively coupled plasma emission spectrometer (ICP-OES, model: Agilent 5110), self-developed chromatographic separation columns, and a switching pulse injection device. The experimental reagents and samples include: HCl at pH=2, 5% mass fraction NaOH solution as a regulator, sodium chloride (NaCl), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), potassium chloride (KCl), and lithium chloride (LiCl), purchased from Shanghai Taitan Technology Co. Uranyl nitrate hexahydrate was purchased from the Institute of Chemical Metallurgy of the Nuclear Industry, Beijing, China. Natural salt lake water was collected from Sugan Lake in Xinjiang with a pH of 8.77, and simulated salt lake water reagent was self-prepared with a pH of 8.5.

We formulated the salt lake simulant with reference to the ion concentration ratio in East Taijinar Salt Lake, China. The major ion concentrations of East Taijinar Salt Lake are shown in Table 1 .

Table 1. Mass fraction of major ions in East Taijinar Salt Lake

Ion	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-
Mass fraction (%)	0.085	5.13	1.47	0.02		

2.2 The Liquid Membrane Theory

Based on previous adsorption studies, Yu concluded that a liquid membrane exists on the adsorbent surface. Solutes in the mobile phase exchange with this liquid membrane, forming an external adsorption/desorption process. Yu subsequently proposed the tidal liquid membrane diffusion model, which was later combined with heterogeneous isothermal adsorption theories to create new kinetic equations (Fig. 1 [Figure 1: see original paper]) [**?**]. This model successfully explains material fluctuations during adsorption/desorption processes [**?**].

We believe that the liquid membrane on the chromatographic packing exchanges solutes with the mobile phase, causing different ions to experience varying degrees of retardation. Therefore, we developed a 10 m pulse column, significantly longer than traditional columns, to achieve ion separation.

2.3 Manufacturing of the Chromatographic Separation Column

In this study, a 10 m silicone tube (5 mm inner diameter, 9 mm outer diameter) serves as the column body, packed with 1.0 mm PMMA pellets for their mechanical strength and chemical stability. To ensure secure connection and permeability, the tube ends are joined to glass fittings using a sand-core embedded design (Fig. 2 [Figure 2: see original paper]). The column packing process is detailed in Supporting Information 1.

2.4 Design of Liquid Flow Switching Controller

This study employed a liquid-air-liquid switching flow mode, with dynamic pulse injection being crucial for nuclide separation. The designed liquid flow switching controller must simultaneously regulate both inlet and outlet sides (Fig. 3 [Figure 3: see original paper]). This instrument uses a dynamic pulse injection system for sample separation and mixing. The sample is injected through the liquid channel for time T_1, followed by air injection for T_2. At the outlet, the sample flows through a mixing channel for T_3, then to the lithium channel for T_4 and the uranium channel for T_5. Once the sample is fully discharged, including the tail portion, the cycle restarts upon detection of a new pulse. The specific operation process of the liquid flow switching controller is described in Supporting Information 2.

2.5 Construction of a Magnetic Field-Assisted Pulsed Liquid Chromatography Device

The overall construction of the magnetic field-assisted pulsed liquid chromatography device is based on the liquid flow-air-liquid flow interval composite flow mode, termed the interval composite flow phase pulse. The entire device comprises five major systems: (1) flow rate control system (power source with peristaltic pump as the core); (2) switching pulse injection/exit system (inlet/exit sample switching device with three-way valve as the core); (3) chromatographic automatic control separation system (chromatography column body with PMMA packing pellets as the core); (4) time control system (incoming/exit time control device with self-developed device as the core); and (5) magnetic field assist system. The overall chromatographic separation device without magnetic field is shown in Fig. 4 [Figure 4: see original paper].

We explored the synergies between these five systems and their independent functions, with special focus on two innovative magnetic field assist systems (shown in Fig. 5 [Figure 5: see original paper]). The first magnetic field assist system involves coiling the column body spirally upward so that the sample solution moves in a spiral upward motion from inlet to outlet. The system is configured peripherally with a horseshoe-shaped magnet, a weak magnet whose peak magnetic field strength was measured by a Gaussmeter to be 4.27 mT. This arrangement utilizes the interaction between helical motion and a weak magnetic field to influence the migration paths and velocities of constituents in the sample solution.

The second magnetic field assist system features an elliptical runway design, where the chromatographic column passes through holes in the center of ring magnets along an elliptical trajectory. Ring magnets are installed every 50 cm. These magnets are made of neodymium-iron-boron material with significant magnetic field strength, peaking at 234.22 mT when measured by a Gaussmeter. This design aims to further enhance selective separation of specific components in the sample through periodically distributed strong magnetic field regions.

2.6.1 Selection of Optimal Separation Conditions

The separation effect of dynamic chromatography is affected by mobile phase pH, flow velocity, and temperature. However, this paper primarily explores simultaneous in situ extraction of U(VI) and Li from salt lakes, so the pH of the salt lake simulation liquid was set to 8.5 (Sugan Lake pH is approximately 8.77 in China). Ye [?] previously conducted related research on assisted kinetic liquid chromatography. We calculated the linear velocity of the sample in the column using Eq 1, and thus derived the sample liquid flow rate of the column.

$$V_{\text{column}} - V_{\text{packings}}$$

Where l (cm/min) is the linear velocity of the solution in the column; Q

(mL/min) is the flow velocity of the solution; H is the length of the column; Vcolumn is the column volume; Vpackings is the total volume of the packings. The flow rate suitable for separation was calculated to be 16 mL/min.

Considering the solution carrying capacity in the column, treatment level, and experimental time cost, the volume of sample for a single pulse injection was controlled to be 20 mL, which matched the injection time of 75 s. To ensure a sufficient distance existed between two pulses, the air intake time was set to 100 s (T_2), and all experiments were conducted at room temperature.

To explore the optimal nodes for extracting U(VI) and Li in a pulse, we designed a detailed sample collection and analysis scheme before multistage separation experiments. The specific steps were as follows: First, ten 10 mL centrifuge tubes were placed at the outlet end. Second, when the first pulse sample liquid began to flow out, 2 mL of sample liquid was collected equally into each centrifuge tube, dividing the pulse into ten parts. Third, this cycle was repeated five times to ensure each centrifuge tube was finally filled with 10 mL of sample fluid. In this way, each centrifuge tube represents a different time point or node of a pulse.

Subsequently, the solutions in these ten centrifuge tubes were analyzed using an inductively coupled plasma emission spectrometer (ICP-OES, model: Agilent 5110) to determine the mass concentrations of Li. By analyzing the concentration trends of each ion, we can determine the specific portion of a pulse that is suitable for extracting U(VI) or Li. Since magnesium-lithium separation is particularly challenging in salt lakes, we paid special attention to the mass concentration ratio of Mg to Li at each node as an important parameter for judging separation effectiveness. This method can not only accurately identify the best extraction nodes but also provide a scientific basis for optimizing subsequent multistage separation experiments. Detailed analysis of different nodes allows more accurate understanding of each ion' s movement state, thereby improving separation efficiency and selectivity.

2.6.2 Multistage Separation Experiments

In this study, simulated salt lake water samples were placed in sample cells. The flow rate control system was activated, and the sample liquid and air were alternately fed into the column in segmented pulses through the switching feed system. Due to the assisted magnetic field and the liquid membrane on the pellets, ion movement in the sample liquid varied, resulting in different peak times for different ions at the outlet. Based on these peak time variations, the outflow channels for $UO_2[CO_3]_3$ and mixed ions were switched.

During one period of pulsed inlet and outlet, the extraction time points for U(VI) and Li were determined. All three channels collected different liquid samples at different times, and the mixed channel sample returned to the sample cell to continue separation until the U(VI) and Li channels accumulated enough enriched liquids to support the next separation stage. Since the experimental steps for U(VI) and Li channels were identical, we take the uranium channel as an example. The nth stage ($n \geq 1$, n is an integer) of enriched liquid collected from the uranium channel was used as the inlet sample for the next (n + 1) stage, resulting in the (n + 1) stage of U(VI) enriched liquid. This process is illustrated in Fig. 6 [Figure 6: see original paper].

III. Results and Discussions

3.1 Column Properties of the PMMA Packings

Polymethyl methacrylate (PMMA) is a polymer material produced by polymerization of methyl methacrylate (MMA) monomer. Due to its excellent corrosion resistance, durability, and good insulating properties, PMMA is widely used in camera lenses, screens, filters, eyeglasses, and decorative materials [**?**, **?**]. In this study, the material was selected to assess the impact of organic functional groups on nuclide separation and for comparative research with inorganic glass. PMMA was chosen for its chemical inertness to salt lake water, resistance to repeated immersion, stability under acid/base conditions, and cost-effectiveness, validating its advantages over traditional inorganic materials.

3.1.1 Characterization of PMMA The PMMA packing was ground to 200 mesh and immersed in the salt lake simulation solution for 24 hours to compare structural and morphological changes before and after the experiment. SEM-EDS characterization (Fig. 7 [Figure 7: see original paper]) revealed a layered structure on the PMMA surface with some tiny holes observable in the overall morphology. EDS spectra showed that PMMA only adsorbed a certain amount of U(VI).

XPS characterization results indicated that the main chemical functional group in PMMA material is the ester group (Fig. 8 Figure 8: see original paper), consistent with the material's chemical structure. A trace amount of magnesium residue remained in PMMA plastic after the experiment, as shown in Fig. 8(b). FTIR analysis (Fig. 8(c)) revealed that the PMMA surface was rich in functional groups, with the vast majority being C-H bonds.

Characterization results show that PMMA molecules lack highly reactive functional groups. The ester group (-COO-) is stable, resistant to hydrolysis, and not prone to chemical reactions. Each repeating unit in the PMMA chain has a methyl ($-CH_3$) side group, giving it a non-polar nature that reduces intermolecular interactions and chemical reactivity. Consequently, PMMA is insoluble in water, resistant to acids and bases, and somewhat resistant to salts. After immersing PMMA pellets in salt lake water for 24 hours, the pellets remained intact. These functional groups did not react with anions and cations such as Ca^{2+} in the solution, supported by the basically consistent trajectories before and after reaction. However, characterization shows that PMMA molecules have a weak adsorption effect on U(VI) and Mg^{2+}.

The non-polar methyl groups in PMMA weaken intermolecular forces and increase chain flexibility. High temperatures may disrupt these forces and alter molecular structure, affecting the physical and chemical properties of PMMA spheres. Therefore, conducting experiments at room temperature ensures the PMMA pellets maintain excellent mechanical strength, allowing the column to withstand multiple pulses of salt lake water and ensuring long service life. With only 20 mL of salt lake simulant per pulse and over 120 L used in total, the column has withstood more than 6000 pulses while maintaining its structure and demonstrating excellent recyclability.

3.2 Distribution of Each Ion in the Column Without Assisted Magnetic Field

In this section, experiments were carried out on organic columns in the absence of a magnetic field to facilitate comparison with subsequent magnetic field addition and with glass inorganic columns, examining the role of functional groups and liquid membrane.

The ion distribution in the PMMA column without magnetic field assistance is shown in Fig. 9 [Figure 9: see original paper]. According to Fig. 9(a), the outflow curve of Li oscillates violently, but the main peak node appears in the first middle part of the pulse (2-10 mL). Based on Fig. 9(c), the first peak of the U/Li ratio occurs at the 10 mL node. In weakly alkaline solutions, U(VI) exists as the uranyl carbonate complex anion ($UO_2[CO_3]_3{}^{4-}$). The motion state of each ion at this time is influenced by the combination of liquid membrane and organic functional groups. However, based on the above characterization, PMMA material has weak adsorption effects on U(VI) and Mg^{2+}, while other ions are unaffected. Moreover, the blocking effect of the liquid membrane is far more pronounced for particles with larger mass than for those with smaller mass. Therefore, U(VI) experiences stronger blocking, causing its peak node to appear later than other ions. The motion state of U(VI) is as expected. However, Li clearly peaks at the front of the pulse. Unlike Li which peaks in the first part of the pulse, Mg shows a slow decline instead. This proves that functional groups and the liquid membrane do exert a longer blocking effect on magnesium, but this effect did not meet our expectations, preventing the achievement of the desired Mg-Li separation effect. Consequently, the Mg-Li ratio shows a gradually decreasing trend (Fig. 9(c)).

If effective Mg-Li separation yields a sufficiently low Mg-Li ratio, the separation node theoretically falls in the post-pulse section (10-20 mL). However, achieving simultaneous U(VI) and Li separation necessitates careful consideration of their respective nodes, as the higher U/Li ratio node also resides in this section (10-20 mL), indicating overlapping extraction windows for U and Li. Consequently, the Li-enriched solution after Mg-Li separation will also contain U(VI), rendering simultaneous extraction of U(VI) and Li impractical without additional influencing conditions (e.g., magnetic field).

3.3 Distribution of Ions in a Horseshoe-Shaped Magnetic Chromatographic Column

Since simultaneous extraction of U(VI) and Li is difficult to achieve without an external field, a horseshoe-shaped magnet was selected as an assisted method. The magnet is weak with low magnetic field strength. According to the magnetic sensor line direction, two sets of experiments were conducted for lateral comparison.

3.3.1 Inward Magnetic Streamlines In this experiment, the 10 m PMMA column was spirally wound from bottom to top to ensure liquid flow moved upward layer by layer. The horseshoe magnets were placed as shown in Fig. 10 Figure 10: see original paper. From the ion concentration change trend plot (Fig. 10(b-c)), the magnetic field had a significant effect on ion motion state. The number of fluctuations for each ion was higher compared to the case without magnetic field. The trends of U(VI) and Li became more similar, as did those of other cations, possibly because under magnetic field action, changes in different ion motion states showed a convergence trend.

According to Fig. 10(d), to achieve Mg-Li separation and extract Li-enriched liquid, we need to choose appropriate separation nodes. Based on the Mg/Li ratio trend, the 2nd-8th mL of the pulse is appropriate as the volume node for Mg-Li separation (where CMg/CLi is relatively low). However, the U/Li ratio trend is reversed. The volume nodes suitable for U-Li separation are at 4th-12th mL. Therefore, half of the volume nodes suitable for Mg-Li separation overlap with half of those suitable for U-Li separation. We believe this is not entirely favorable for achieving simultaneous separation and extraction of U(VI) and Li. Consequently, multistage separation experiments will not be assisted by this type of magnetic field.

3.3.2 Outward Magnetic Streamlines The previous magnetic field configuration failed to achieve ideal simultaneous extraction of U(VI) and lithium, prompting an adjustment to direct magnetic field streamlines outward from the center. This change aimed to optimize ion movement and improve separation efficiency and selectivity for U(VI) and lithium. However, the expected amplification of ion motion differences was not observed (Supporting Information 3), and the volume nodes for extracted Li and U(VI) still overlapped. This is likely due to the weak magnetic field strength of the horseshoe magnet, which had limited effect on ion motion within the column. Therefore, this magnetic field-assisted approach is also unsuitable for multistage separation experiments.

3.4 Distribution of Ions Under the Action of Ring Magnets

In chromatographic separation experiments, a strong magnetic ring was introduced to enhance the weak magnetic field’ s influence on ion behavior. Contrast experiments using two configurations based on the magnetic ring’ s pole direction were conducted. The magnetic rings were uniformly spaced at 50 cm intervals along the column' s axial direction to ensure consistent polarization. Two arrangements were tested: the "S-N" arrangement (Fig. 11 Figure 11: see original paper) and the "N-S" arrangement (Fig. 11(b)), to explore the effect of magnetic field direction on chromatographic separation.

3.4.1 Ion Distribution of the "S-N"Type Arrangement According to Fig. 12 [Figure 12: see original paper], the assisted magnetic field had a significant effect on the motion state of ions in the column effluent. Fig. 12(a) clearly shows that most Li appears in the pre-pulse segment, while the main peak of U(VI) is in the post-pulse segment (12th-20th mL). Comparing with Fig. 9(a), more Li is found in the pre-pulse segment and $UO_2[CO_3]_3$ is more concentrated in the post-pulse segment. This indicates that under ring magnet influence, Li motion is accelerated while $UO_2[CO_3]_3$ motion is slowed down. According to Fig. 12(c), the Mg/Li ratio remains at a low level from the 2nd to 16th mL, which is suitable for Mg-Li separation and Li extraction, while the main peak of U/Li ratio is obviously at 10th-20th mL.

Taken together, this magnetic field-assisted approach is suitable for simultaneous extraction of U(VI) and Li. Without affecting the extraction efficiency of both, we averaged the separated volumes as much as possible. Therefore, the 2nd-10th mL of the pulse was taken as the Li extraction portion (exiting from the Li channel), and the 10th-18th mL was used as the U(VI) extraction portion (exiting from the U(VI) channel). Since the last fraction of a pulse is mixed with air, the flow rate becomes very fast, which we believe affects experimental data and is therefore unsuitable for collection (18th-20th mL).

3.4.2 Ion Distribution of the "N-S" Type Arrangement Compared with the "S-N" arrangement results, experimental results showed significant differences when the ring magnet direction was reversed (i.e., the "N-S" arrangement). Most notably, the motion states of various ions became highly similar, making simultaneous extraction of Li and U(VI) difficult. According to data in Fig. 13 Figure 13: see original paper and Fig. 13(c), under this magnetic field configuration, high-mass uranyl ions peaked at the front of the pulse. Simultaneously, Li was collided and squeezed by massive ions such as uranyl carbonate at the front end, showing greater and more frequent volatility in its peak emergence trend. Furthermore, three distinct fluctuations in the Mg/Li mass concentration ratio occurred during this process, which were unfavorable for multistage separation experiments. In contrast, Fig. 13(b) and Fig. 13(d) show extremely similar peak-out states for remaining cations. Overall, this assistance was not conducive to our separation experiments.

The significant difference between "S-N" and "N-S" arrangements was primarily due to the change in magnetic field polarity. Although the liquid membrane remained intact throughout the experiment and the magnetic field did not damage its surface, the magnetic field direction notably influenced ion motion in the column. Specifically, polarity change affected ion migration paths and velocities, thereby impacting overall separation efficiency.

In summary, based on experimental results from two magnet types and four magnetic field assisting methods, the "S-N" type assistance using ring magnets is most conducive to realizing simultaneous extraction of U(VI) and Li from salt lakes.

3.5 Distribution of Ions in an Inorganic Glass Chromatographic Column

In this section, using a column equipped with glass packing, we demonstrated not only the magnetic field effect but also verified the presence of a liquid membrane. The validation results were contrasted with those from Section 3.2, further confirming the influential role of organic functional groups.

3.5.1 Distribution of Ions in the Column Without Assisted Magnetic Field In the glass column, the motion behavior of most ions showed similar characteristics, while the Mg/Li ratio gradually increased with time and the U/Li ratio showed large fluctuations (Supporting Information 4 Fig. 2). This demonstrates that in the absence of any effect from the glass packing itself on Li and Mg, the trend in the Mg/Li ratio accounts for Li peaking earlier than Mg (a gradual increase in the Mg/Li ratio overall, Supporting Information 4 Fig. 2c). This verifies the role of the liquid membrane, which is less effective in blocking Li than the larger mass of Mg^{2+}. In contrast, according to data in Fig. 9, the Mg/Li ratio trend in the PMMA pellet column was opposite to that in the glass column. Regarding the reason for this variability between the two columns in a non-magnetic field environment, we believe it is caused by different functional groups and their properties on the surfaces of different packing pellets.

3.5.2 Ion Distribution of the "S-N" Type Arrangement (Ring Magnet) When the ring magnet was arranged around the glass column in the "S-N" configuration, the difference in ion motion states under the strong magnetic field became significant compared to the case without magnetic field assistance (Supporting Information 4 Fig. 3). This result was consistent with our study of magnetic field effects using the PMMA pellet column, suggesting the universality of magnetic field effects on ion behavior. However, the glass column under the ring magnet did not show the expected improvement in extraction efficiency for U(VI) and Li. This indicates significant differences in optimal enabling assistance strategies for effective separation and extraction for columns of different materials. Therefore, selecting assisted methods and column packing materials suitable for specific applications is crucial to optimize the separation process.

This study found that PMMA material is more effective than ordinary glass and more suitable for multistage separation experiments for simultaneous extraction of U(VI) and Li from salt lakes.

3.6 Multistage Separation Experiments by the PMMA Column

To further clarify the separation process, for each 2-mL node volume, we artificially recorded the corresponding time nodes and summarized these data in Table 2 . Based on this time node data, we used the time control shunt to accurately direct each outflow from the correct outlet of a pulse according to peak onset time differences. This method not only improved experimental operability and accuracy but also effectively solved challenges caused by volume measurement uncertainty. This ensured that different ions (such as U(VI) and Li) were accurately separated and collected into corresponding channels during specific time periods, optimizing the classification experiment effect for simultaneous extraction of U(VI) and Li.

Table 2. The time nodes corresponding to each volume node

Volume nodes (mL)	0	2	4	6	8	10	12	14	16	18	20
Time nodes (s)											

The separation effect of multistage separation experiments was judged by the separation factor. The calculation formula of the separation factor is shown in Eq 2:

$$\alpha_n = \frac{B}{A}$$

Where, for Mg-Li separation, since Mg/Li is gradually decreasing, to ensure the separation factor is positive, A represents the concentration ratio of Mg to Li in the initial solution, and B represents the concentration ratio of Mg to Li in the solution after separation. For U-Li separation, B represents the concentration ratio of $UO_2[CO_3]_3$ to Li in the initial solution, and A represents the concentration ratio of $UO_2[CO_3]_3$ to Li in the solution after separation; α is the separation factor; n is the number of separation stages.

When the separation factor is largest, the separation effect is most significant, and the theoretical separation stage corresponding to the separation extraction can be calculated according to the optimal separation factor and industrial demand.

Based on the above results, multistage separation and extraction experiments were carried out with the "S-N" type ring magnetic field-assisted chromatographic column. As seen from Section 3.4.1, 14-58 s and 58-87 s were set as the times when effluent flowed out from the lithium channel and uranium channel, respectively, with effluent flowing from the mixed channel during remaining times.

The experimental results are shown in Fig. 14 [Figure 14: see original paper]. In the five-stage separation experiments of the lithium channel (Fig. 14(a-b)), the Mg-Li separation effect was basically consistent with our expectations, and the overall Mg/Li ratio showed an obvious decreasing trend. According to Eq 2, the corresponding separation factors for each stage were calculated, taking the first stage as the base. The results clearly indicated that the separation factor reached its maximum at the third stage, which was 1.202, representing the best separation effect at this point. The Mg/Li ratio in Chinese salt lakes can span from tens to thousands [**?**], and since higher Mg/Li ratios increase Li purification difficulty, researchers have focused on lowering the Mg/Li ratio in brine. When the Mg/Li ratio in high Mg/Li ratio salt lake brines (65.6) was reduced below 20, the interference of Mg on Li extraction became relatively small [**?**], significantly improving Li extraction efficiency and purity while reducing production costs. Taking a salt lake water sample with an initial Mg/Li ratio of about 200 as an example, reducing this ratio to 20 corresponds to a theoretical requirement of 13 separation stages according to Eq 2.

In the five-stage separation experiments of the uranium channel (Fig. 14(c-d)), the separation effect of U(VI) and Li was consistent with our expectations. The overall U(VI)/Li ratio showed an obvious upward trend, and the maximum separation factor reached 1.088, proving that the separation efficiency of U(VI) and Li was significantly lower than that of Mg and Li.

In conclusion, we compared separation effects under three auxiliary methods: no magnet, horseshoe magnet, and ring magnet. The separation factors for these three methods were calculated for reference (Table 3). It is obvious that the PMMA column can realize simultaneous extraction of U(VI) and Li with the assistance of a strong magnetic ring.

Table 3. Table of separation factors for different auxiliary methods

Auxiliary method	α_1 (separation factor) (Mg-Li)	α_2 (separation factor) (U-Li)
Non-magnetic		
Horseshoe Magnet		
Ring magnet ("S-N")		

3.7 Mechanism of Separation by Ring Magnetic Field-Assisted Chromatography

3.7.1 Preliminary Discussion Based on Experimental Results This study confirms that when a solution moves through a column, elements exist as charged ions. Ignoring quantum effects, charged ions are influenced by the Lorentz force in the magnetic field, as their movement is directly affected by the magnetic field' s presence, which differs significantly from a state without a magnetic field. Thus, to a certain extent, the original state of motion will be changed. The force on charged particles in the magnetic field can be expressed using Eq 3 [?]. The Lorentz force FL acting on an ion with charge q can be expressed as a function of the electric field E (V/m) and the cross product between the ion velocity v and magnetic field B (T):

$$F_L = q(E + v \times B)$$

When magnetic rings are arranged in the "S-N" type, cations interact with the liquid membrane on the packing surface, their diagonal forward trajectory cuts the streamlines, and the Lorentz force has a component on the cations in the direction of macroscopic liquid flow motion. Meanwhile, anions such as $UO_2[CO_3]_3{}^{4-}$ are subjected to a component force opposite to the motion direction under the effect of the liquid membrane and Lorentz force, so the peak time of $UO_2[CO_3]_3{}^{4-}$ is delayed.

When magnetic rings are arranged in the "N-S" type, contrary to the above, $UO_2[CO_3]_3{}^{4-}$ is subjected to a partial force in the same direction as the macroscopic liquid flow motion, causing $UO_2[CO_3]_3{}^{4-}$ to peak earlier at the front end of the pulse. Due to excessive accumulation of uranyl ions at the front end, Li^+ ions also accumulate there, resulting in peak crossing with uranyl ions.

3.7.2 In-Depth Analysis of Liquid Membrane and Magnetic Field Effects Further analysis based on Fig. 15 [Figure 15: see original paper] shows that F0 is the thrust generated by the peristaltic pump. From a macroscopic perspective, the flow rate of a pulse section is constant, so Li^+ and $UO_2[CO_3]_3{}^{4-}$ are subjected to the same magnitude of thrust. Under conditions without magnetic field influence, Li^+ and $UO_2[CO_3]_3{}^{4-}$ are subjected to constant thrust. As they penetrate the liquid membrane, they experience different magnitudes of blocking forces until they exit the liquid membrane again. This blocking force on $UO_2[CO_3]_3{}^{4-}$ is greater than that on Li^+, which can be referred to the liquid membrane diffusion model shown in Fig. 1.

Under the influence of the "S-N" toroidal magnetic field (Fig. 15), the magnetic field force is F2. Ion movement within a single separation unit can be divided into two stages. The first stage (initiation stage): Li^+ and $UO_2[CO_3]_3{}^{4-}$ approach the S-pole of the magnet and are subject to the same peristaltic pump thrust magnitude. However, due to their charge difference, the magnetic poles produce opposite directions. The ion motion direction forms a certain angle with magnetic induction. At this point, the S pole of Li^+ is close to the S pole of the circular magnet, mainly producing repulsive force (partial force manifested as forward thrust and upward force), increasing Li^+ speed. The N pole of $UO_2[CO_3]_3{}^{4-}$ is close to the S pole of the circular magnet, mainly producing attractive force (partial force manifested as backward pulling force and upward force), slowing down $UO_2[CO_3]_3{}^{4-}$ speed.

The second stage (liquid membrane intervention stage): Li^+ and $UO_2[CO_3]_3{}^{4-}$ penetrate the liquid membrane and interact with it, both beginning to experience different magnitudes of blocking force while the rest of the state remains basically similar to the first stage. When ions move to the highest or lowest point of the liquid membrane, they gradually penetrate out of the liquid membrane following the tangent line, and the process repeats the first and second stages.

Overall, under this magnetic field environment, Li^+ receives more forward thrust while $UO_2[CO_3]_3{}^{4-}$ receives more backward resistance. The blocking effect of the liquid membrane on $UO_2[CO_3]_3{}^{4-}$ is greater than that on Li^+. Therefore, under the "S-N" ring magnetic field influence, Li^+ peaks before U. This explains why when the magnet is placed in the ring, Li peaks before $UO_2[CO_3]_3{}^{4-}$, and why flipping the magnet poles to the "N-S" type produces opposite ion motion states.

3.7.3 Preliminary Calculations on Forces on Ions Since results under the two strong magnetic ring aids are quite different and the "S-N" type aid is more effective, we calculated specific force values under both magnetic ring assistance types ("S-N" and "N-S") to enhance mechanistic explanation. Taking Li^+ as an example, we used Newton' s second law to calculate acceleration based on its corresponding peak-out time without magnetic field assistance (tLi0), with "S-N" type (ta) and "N-S" type (tb) magnetic field assistance, as well as the corresponding forces (detailed calculations are given in Supporting Information 5).

To facilitate calculation of time differences, we created a concept called half-concentration flux (Supporting Information 6). We calculated the magnitude of force on an ion in a magnetic field, which is close to the magnitude Ye calculated in his work (10 N) for ion interactions with liquid membranes [?]. This proves that the effects of liquid membrane hysteresis and Lorentz force cannot be neglected.

In summary, with the "S-N" configuration, Li^+ experiences Lorentz force in the same direction as its motion, while $UO_2[CO_3]_3{}^{4-}$ moves in the opposite direction. In the "N-S" configuration, $UO_2[CO_3]_3{}^{4-}$ moves in the same direction as its motion, and Li^+ moves in the opposite direction. The magnetic forces on $UO_2[CO_3]_3{}^{4-}$ are greater than those on Li^+, likely due to its higher mass and charge, enabling effective simultaneous separation and extraction of U(VI) and Li.

IV. Conclusions

In this study, PMMA pellets were utilized for the first time as packing material in a pulse injection chromatographic column and applied to the in situ extraction of U(VI) and Li resources from salt lake water with magnetic field assistance.

1. Characterization by SEM-EDS, XPS, and FTIR shows that PMMA material is stable in nature with good mechanical strength and long service life. It is more effective than glass material in experiments due to abundant

functional groups. The physical and chemical properties of the PMMA column remained unchanged after enduring more than six thousand pulse experiments, and its good cycling performance makes it suitable for studying simultaneous separation and extraction of U(VI) and Li from salt lakes.

2. Two different magnet types and their arrangements were explored to enhance separation, and optimal chromatographic separation conditions and time points were determined. The results show that ring magnets have better assisting effects and can realize simultaneous separation and extraction of U(VI) and Li. In five-stage separation experiments assisted by ring magnets, the Mg-Li separation factor reached up to 1.202, and the U(VI)-Li separation factor reached 1.088, proving that efficient simultaneous extraction of U(VI) and Li from salt lake water simulated liquid has been successfully realized.
3. The reasons for differences in ion motion states under ring magnet action were discussed, providing theoretical basis and technical support for future simultaneous extraction of U(VI) and Li from high Mg/Li ratio salt lake resources. The present study further validates the presence of liquid membrane. The innovative pulse chromatography method was successfully applied to salt lake resource extraction, proving its innovation, economy, and environmental friendliness, and providing valuable data.

V. References

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